

Aberystwyth University

Origin and fate of Vanadium in the Hazeltine Creek Catchment following the 2014 Mount Polley mine tailings spill, British Columbia, Canada

Hudson-Edwards, Karen A.; Byrne, Patrick; Bird, Graham; Brewer, Paul; Burke, Ian; Jamieson, Heather; Macklin, Mark; Williams, Richard

Published in:
Environmental Science & Technology

DOI:
[10.1021/acs.est.8b06391](https://doi.org/10.1021/acs.est.8b06391)

Publication date:
2019

Citation for published version (APA):
Hudson-Edwards, K. A., Byrne, P., Bird, G., Brewer, P., Burke, I., Jamieson, H., Macklin, M., & Williams, R. (2019). Origin and fate of Vanadium in the Hazeltine Creek Catchment following the 2014 Mount Polley mine tailings spill, British Columbia, Canada. *Environmental Science & Technology*.
<https://doi.org/10.1021/acs.est.8b06391>

General rights

Copyright and moral rights for the publications made accessible in the Aberystwyth Research Portal (the Institutional Repository) are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the Aberystwyth Research Portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the Aberystwyth Research Portal

Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

tel: +44 1970 62 2400
email: is@aber.ac.uk

Characterization of Natural and Affected Environments

Origin and fate of Vanadium in the Hazeltine Creek Catchment following the 2014 Mount Polley mine tailings spill, British Columbia, Canada

Karen A. Hudson-Edwards, Patrick Byrne, Graham Bird, Paul A. Brewer,
Ian T. Burke, Heather Jamieson, Mark Macklin, and Richard Williams

Environ. Sci. Technol., **Just Accepted Manuscript** • DOI: 10.1021/acs.est.8b06391 • Publication Date (Web): 04 Mar 2019

Downloaded from <http://pubs.acs.org> on March 14, 2019

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

Origin and fate of Vanadium in the Hazeltine Creek Catchment following the 2014 Mount Polley mine tailings spill, British Columbia, Canada

Karen A. Hudson-Edwards^{1}, Patrick Byrne², Graham Bird³, Paul A. Brewer⁴, Ian T. Burke⁵, Heather E. Jamieson⁶, Mark G. Macklin⁷, Richard D. Williams⁸*

¹ Environment & Sustainability Institute and Camborne School of Mines, University of Exeter, Penryn, Cornwall TR10 9FE, UK. *Corresponding author. Email k.hudson-edwards@exeter.ac.uk; Tel: +44-(0)1326-259-489.

² School of Natural Sciences and Psychology, Liverpool John Moores University, Liverpool, L3 3AF, UK. Email p.a.byrne@ljmu.ac.uk

³ School of Environment, Natural Resources and Geography, Bangor University, Bangor, Gwynedd, LL57 2UW, UK. Email: g.bird@bangor.ac.uk

⁴ Department of Geography and Earth Sciences, Aberystwyth University, Penglais, Aberystwyth, Ceredigion WY23 3FL, UK. pqb@aber.ac.uk

⁵ School of Earth and Environment, University of Leeds, Leeds LS2 9JT, UK. i.t.burke@leeds.ac.uk

⁶ Department of Geological Sciences and Geological Engineering, Queen’s University, Kingston, Ontario K7L 3N6, Canada. jamieson@queensu.ca

⁷ Lincoln Centre for Water and Planetary Health, School of Geography, College of Science, University of Lincoln, Brayford Pool, Lincoln, Lincolnshire LN6 7TS, UK. mmacklin@lincoln.ac.uk

⁸ School of Geographical and Earth Sciences, University of Glasgow, Glasgow G12 8QQ, UK. Richard.Williams@glasgow.ac.uk

Submitted to: *Environmental Science & Technology*

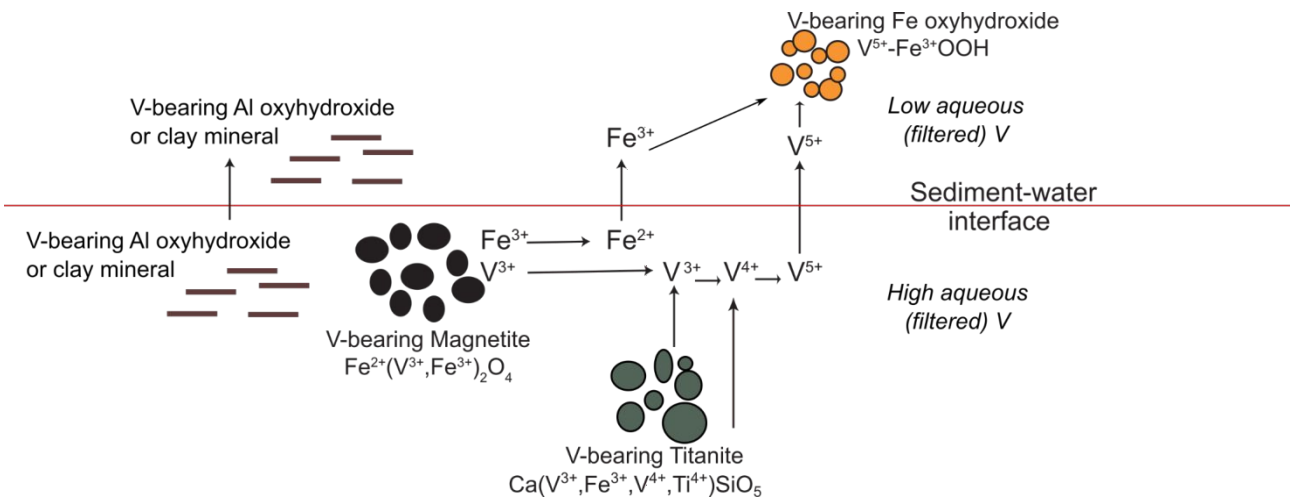
Date of 2nd re-submission: 1 March 2019

Keywords: Vanadium; Mount Polley; tailings; magnetite; titanite; XANES

ABSTRACT

Results are presented from the analysis of aqueous and solid-phase V speciation within samples collected from the Hazeltine Creek catchment affected by the August 2014 Mount Polley mine tailings dam failure, Canada. Electron microprobe and XANES analysis found that V is present as V^{3+} substituted into magnetite, and V^{3+} and V^{4+} substituted into titanite, both of which occur in the spilled Mount Polley tailings. Secondary Fe oxyhydroxides forming in inflow waters and on creek beds have V K-edge XANES spectra exhibiting $E_{1/2}$ positions and pre-edge features consistent with the presence of V^{5+} species, suggesting sorption of this species on these secondary phases. PHREEQC modelling suggests that the stream waters mostly contain V^{5+} , and the inflow and pore waters contain a mixture of V^{3+} and V^{5+} . These data, and stream, inflow and pore water chemical data, suggest that dissolution of V(III)-bearing magnetite, V(III,IV)-bearing titanite, V(V)-bearing Fe(-Al-Si-Mn) oxyhydroxides, V-bearing $Al(OH)_3$ and/or -clay minerals may have occurred. In the circumneutral pH environment of Hazeltine Creek elevated V concentrations are likely naturally attenuated by formation of V(V)-bearing secondary Fe oxyhydroxide, $Al(OH)_3$ or clay mineral colloids, suggesting that the V is not bioavailable. A conceptual model is presented describing the origin and fate of V in Hazeltine Creek that is applicable to other river systems.

43 ToC Art



44
45
46

47 INTRODUCTION

48 Vanadium (V) is a transition metal which is the 22nd most abundant in the Earth's crust^{1,2} and
49 occurs naturally in four oxidation states (V(II), V(III), V(IV) and V(V)). Although V is an essential
50 element for humans and animals at low concentrations³, intake of high concentrations of V can be
51 carcinogenic and toxic^{4,5}. Generally V(V) is considered to be the most toxic of the V species because
52 it can inhibit or replace phosphate^{6,7}. Vanadium is classed by the United Nations, US Environmental
53 Protection Agency and Chinese Ministry of Environmental Protection as a priority environmental risk
54 element^{2,8,9,10}. In recognition of the potential toxicity of V, Canada has set a Federal Water Quality
55 Guideline of 120 µg/L for protection of aquatic life in freshwater¹¹, and Schiffer and Liber¹² have
56 suggested a more stringent chronic hazardous concentrations endangering only 5% of species (HC5)
57 of 50 µg/L for Canadian freshwater organisms.

58 Humans can be exposed to vanadium mainly through inhalation and ingestion, potentially
59 causing long-term respiratory and digestive problems, respectively¹³. Aqueous vanadate (V(V)) can
60 also be taken up in benthic organisms such as *Hyalella azteca*¹⁴, and have been shown to cause
61 genotoxic and cytotoxic effects in higher plants¹⁵. Vanadium can be distributed in water, soil,
62 sediment and air through the weathering of natural materials and through releases from anthropogenic
63 activities including the burning of fossil fuels, application of pesticides and phosphate fertilizers, steel,
64 aerospace and other industries, and mining^{9,16,17}. For example, mining activities have led to
65 contamination of waters and soils with V (e.g., 76-208 µg/L in groundwaters and 149 to 4800 mg/kg
66 V in soils of the Panzhihua mining and smelting area, China^{18,19}). There is, however, a lack of
67 information on, and understanding of, the geochemical-mineralogical cycling of V in mining-affected
68 environments²⁰, but these are required to determine health effects and to develop management and
69 remediation schemes.

70 Mine tailings dam failures can rapidly add large amounts of V-bearing solid and liquid wastes
71 to the fluvial environment²¹. Globally, failures of mine tailings dams impact significantly in the short-
72 (hours to months) and long-term (years to centuries) on ecosystems and humans that live in affected

catchments, through erosion, deposition of tailings sediment and fluids, contamination of soil and water with potentially toxic metal and metalloid elements, and loss of life^{22,23}. The 4th August 2014 failure of the tailings storage facility (TSF) at Mount Polley, British Columbia, Canada, is the second-largest by volume on record²³. Approximately 25 Mm³ of material, comprising 7.3 Mm³ of tailings solids, 10.6 Mm³ of supernatant water, 6.5 Mm³ interstitial water and 0.6 Mm³ of, tailings dam construction materials were discharged into the Quesnel River Watershed²³⁻²⁵. The material flowed north into and plugged Polley Lake, then was diverted south-east into Hazeltine Creek for 9.5 km. A significant proportion of the tailings and interstitial water ($18.6 \pm 1.4 \text{ M m}^3$; ²⁵) and eroded soils and vegetation²⁶ were deposited into the West Basin of Quesnel Lake (Figure 1). Deposition of tailings (average 1 m thick, but up to 3.5 m thick in the upper part of the area nearest the TSF) also occurred within the Hazeltine Creek catchment up to 100 m from the channel, especially near Polley Lake and Lower Hazeltine Creek²⁵. Extensive clean-up has been undertaken since the spill (and since the sampling for this study was undertaken), comprising removal of most of the spilled tailings from, and restoration of, the catchment. This was aimed at restoring ecosystem habitats through the establishment of a new rock-lined channel, reducing remobilization of the remaining tailings and exposed natural sediments and decreasing turbidity.^{27,28}.

Mount Polley is a Cu-Au porphyry deposit, and the tailings comprise mostly silicate minerals (feldspars, ferro-magnesian and Ca-Ti-silicates, muscovite), oxides such as magnetite and rutile, carbonates, Cu sulfides and pyrite. Although the Mount Polley tailings have low sulfide (0.1 – 0.3 wt. %) and trace metal and metalloid concentrations²⁹ relative to other tailings^{22,30,31}, they have elevated concentrations of V (86 – 295 mg/kg) compared to local background soils (40.2 – 133 mg/kg²⁶). Vanadium was also initially identified, in addition to Cu, Se and Mo, as a contaminant of potential concern in Hazeltine Creek soils³². The cycling of Cu in Hazeltine Creek has been previously examined in detail^{26,29,33-37}, but detailed geochemical and mineralogical studies of V, Se and Mo have not been conducted.

In this paper we focus on V due to its high environmental risk potential^{2,8,9,10} and to the relative lack of data on its behavior in mining-affected environments²⁰. We aim to understand the geochemical cycling of V in the Hazeltine Creek catchment and its implications for the origin, transport, fate and potentially toxicity of V in other river systems. The objectives of the study are to determine (1) V concentrations and speciation in stream, inflow and pore waters using aqueous composition data and PHREEQC modeling, (2) solid-phase V concentrations and speciation in the deposited tailings and secondary Fe oxyhydroxides using electron microprobe, automated mineralogy analysis and X-ray absorption spectroscopy (XAS) analysis, (3) the environmental origin, fate and potential hazard of the deposition of V-bearing tailings in mining-affected catchments following tailings dam failures and remediation. We present, for the first time to our knowledge for natural systems, evidence that dissolution of V-bearing magnetite and titanite may contribute to aqueous V. The results will also inform restoration and management schemes for river systems receiving V from other natural and anthropogenic sources.

MATERIALS AND METHODS

Field Site. The Mount Polley porphyry Cu-Au mine³⁸ is located in British Columbia, Canada, 275 km south-east of Prince George (Figure 1). Hazeltine Creek drains an area of 112 km², including Polley Lake (Figure 1), and flows 9.5 km in a south-easterly direction before discharging into Quesnel Lake. Hazeltine Creek has an alkaline pH (average 8.2 prior to the spill³⁹; 7.0-9.3 from 30th July to 2nd August 2015³⁷). The catchment is underlain by Late Triassic alkali intrusions, including the porphyry Cu-Au orebody, and by Mesozoic basaltic and andesitic volcanics, and glaciofluvial and glaciolacustrine deposits³⁸.

Water Sampling, Analysis and Speciation-Solubility modelling. Details of water sampling analysis and quality control are presented in Byrne et al.³⁷ and are summarized briefly here. In August 2015 sample collection comprised from 10 stream waters from Hazeltine Creek, 12 inflow waters seeping from riparian tailings into the creek, and 3 stream channel pore water sites collected at 10

and 20 cm depth through deposited tailings, natural stream sediments and bank materials (using a 3/8" stainless steel piezometer and peristaltic pump). The piezometer design used in this study was developed by the U.S. Geological Survey and has been used extensively to sample trace metals in pore waters. Standard practice for operating the piezometer is to flush with deionized water before and after pumping to ensure that the drive point itself is clean and not contaminated. Furthermore, it is unlikely that metal leaching would occur over the timescale of pore water pumping / sampling (2 – 3 min). Thus, we believe that there was no contribution of V or other metals to the pore water samples. The sampling took place when spilled tailings were being excavated and removed from the creek valley, creek turbidity was high and a new channel was being constructed. Thus, the results reported here could be considered to represent conditions that might be encountered during a spring freshet³⁴. The concentrations of total and filtered (<0.45 μm) major (Al, Ca, K, Mg, Na, Si) and trace elements (As, Cd, Cu, Cr, Fe, Mo, Mn, Ni, Pb, Se, V, Zn) were determined by inductively coupled plasma – optical emission spectroscopy (Thermo Scientific iCAP 6500 Duo) and – mass spectroscopy (Thermo X-series 1), respectively. Ion chromatography (Dionex ICS-2500) was used to determine filtered anion (Cl, F, SO_4) concentrations. Equilibrium modeling, using the measured aqueous concentrations and other aqueous parameters of the Hazeltine Creek stream, inflow and pore water samples, were carried out using the PHREEQC code and the minteq.dat.v4 thermodynamic database distributed with the code^{40,41}. Alkalinity was estimated for the stream and inflow waters as bicarbonate by ion sum calculation (i.e., charge balanced was forced with bicarbonate). We carried out calculations to check if the modelled V speciation and saturation indices were sensitive to bicarbonate activity using different HCO_3 concentrations and found no significant differences in our results. Ferrihydrite and amorphous $\text{Al}(\text{OH})_3$ were allowed to precipitate during the equilibrium modeling, as the waters are not likely to be very much oversaturated with respect to these minerals.

Tailings, Sediment and Fe oxyhydroxide Sampling and XRF V Analysis. In August 2016 samples of deposited tailings and a secondary Fe oxyhydroxide sample deposit scraped from a seep draining a re-profiled stream bank (Supplementary Table S4) were also collected in clean

polyethylene bags. These were air-dried and stored at 4 °C until used. A proportion was crushed and pressed into powder pellets for V analysis by XRF (Bruker S4 Pioneer). Sub-samples of deposited tailings (ST 09-02-01-140915 and WT 17-08-02-140912; Supplementary Table S4) collected in 2014 following the dam failure by consultants of Mount Polley Mining Corporation, and described in SNC-Lavalin Inc²⁶, were donated by the mine for comparison to samples collected by the authors.

Electron Microprobe and Automated Mineralogy Analysis. Polished blocks of all solid samples were examined with a Jeol 8100 Superprobe (WDS) with an Oxford Instrument Inca System (EDS). Spot analyses and X-ray chemical mapping were carried out by collecting energy data between 0 and 20 eV using a 15 kV accelerating voltage, 2.5 mA current and a spot size of 1 µm. The analyses were calibrated using a ZAF (atomic number, absorption, fluorescence) matrix correction with standards of oxides and Specpure metals. To quantify and further characterize and quantify the bulk mineralogy and those minerals identified with the Superprobe as containing V, the polished blocks were investigated using an Mineral Liberation Analysis automated mineralogy system on a FEI Quanta 650 FEG ESEM equipped with twin Bruker XFlash EDS detectors at Queen's University, Canada. Spectra were collected at 25kV, with a minimum of 2000 counts per analysis, collecting 250,000+ X-ray spectra on each sample to calculate total area percentages of each mineral detected, then a further 800,000 spectra at higher resolution searching and targeting V-bearing minerals at fine detail.

X-ray Absorption Spectroscopy (XAS) Analysis. Microfocus XANES V K-edge spectra (5465 eV) for individual magnetite, titanite and Fe oxyhydroxide grains were collected on beam line I18 at the Diamond Light Source operating at 3 GeV with a typical current of 300 mA, using a nitrogen cooled Si(111) double crystal monochromator and focusing optics. Kirkpatrick-Baez mirrors were used to produce a focused beam of 3 µm diameter at the sample. For samples and standards (V metal, V₂O₃, VO₂, V₂O₅, V(V) sorbed to FeOOH (see SI for preparation method)), K-edge spectra were collected in fluorescence mode at room temperature (~295 K) using a 4 element solid state Si detector. Because we analyzed V-bearing titanite we checked that the V K α emission

line could be resolved, despite its overlap with the Ti K β emission line. On beamline I18, the Ti K α emission at ~ 4510 eV is resolvable in XRF detectors from the V K α emission at ~ 4950 eV (250-300 eV separation is required for effective windowing of I18's XRF detectors). The lower intensity Ti K- β emission at 4932 eV is not resolvable by any XRF detector but the binding energy of the V-K edge (5465 eV) is about 500 eV above the Ti K-edge (4966 eV). Therefore, interference of the Ti K- β XAS spectra and V K- α XANES spectra was minimal and limited to long wavelength, low amplitude EXAFS oscillations, by 4950 eV Ti k-edge oscillations that would be not be apparent in V-XANES. After collecting the XANES data, multiple scans were then averaged to improve the signal to noise ratio using Athena version v0.8.061⁴². XANES spectra absorption data were also normalized in Athena over the full data range and plotted from approximately -15 eV to +30 eV relative to the edge position with no correction required for drift in E_0 . Vanadium data were calibrated using E_0 measured from thin metal foils inserted downstream of the samples and measured simultaneously. The V-metal K-edge was detected and the E_0 position did not drift between spectra. The V pre-edge peak energy was determined by calculation of the area normalized centroid energy position (i.e., the peak intensity is normalized to the height of the main V K-edge step on the y-axis of the resultant graph, plotted against the area normalized pre-edge centroid peak energy position on the x-axis) following the method of Chaurand et al.⁴³, and used previously for solid-phase V speciation in bauxite residue⁴⁴.

RESULTS AND DISCUSSION

Aqueous V geochemistry and speciation. Filtered V concentrations (mean: 9 $\mu\text{g/L}$; range: 7 – 12 $\mu\text{g/L}$) in the Hazeltine Creek stream waters were slightly elevated compared to pre-event mean concentrations (1 $\mu\text{g/L}$ ²⁹), higher than mean global filtered river concentrations (0.71 $\mu\text{g/L}$ ⁴⁵), but lower than chronic hazardous concentrations recently identified for freshwater organisms¹².

Overall, filtered V concentrations declined with distance downstream of the Polley Lake weir (Figure 2). Filtered V concentrations in the stream waters were generally lower than those of the

202 inflows seeping from tailings (mean: 17 $\mu\text{g/L}$; range: 4 – 41 $\mu\text{g/L}$), but the inflow waters do not
203 appear to have affected V concentrations downstream, likely because of their low volumes and flow
204 rates (Figure 2). Unfiltered V concentrations in stream (mean: 15 $\mu\text{g/L}$; range: 11 – 21 $\mu\text{g/L}$) and
205 inflow waters (mean: 59 $\mu\text{g/L}$; range: 4 – 303 $\mu\text{g/L}$ ¹) were either similar to (within 7 $\mu\text{g/L}$; 62% of
206 samples) or higher than (up to 278 $\mu\text{g/L}$; 38% of samples) their respective filtered concentrations³⁷.
207 Unfiltered V concentrations were highest in the inflow waters in the upper part of the catchment
208 within approximately 2000 m of the Polley Lake weir (Figure 2).

209 Filtered V concentrations in the Hazeltine Creek stream waters at 0 cm in the sampled profiles
210 (8 – 11 $\mu\text{g/L}$) were similar to those of the other stream waters collected. At 10 cm depth all filtered
211 pore water V concentrations peaked (132, 1200 and 53 $\mu\text{g/L}$ for PW-1, PW-2 and PW-3, respectively;
212 Figure 3), but concentrations declined at 20 cm depth (83, 231 and 43 $\mu\text{g/L}$ for PW-1, PW-2 and
213 PW-3, respectively). Peaks in filtered V concentrations at 10 cm depth coincide with peaks in filtered
214 Al, As, Ca, Cu, Fe, K, Mg, Mn, Ni, Zn and Si, and declines in ORP and pH (Figure 3). The fact that
215 PW-2 has higher V concentrations than those in PW-1 and PW-3 might be due to its position at the
216 downstream end of upper Hazeltine Creek (Figure 1), where the greatest amount of spilled tailings
217 were deposited following the tailings dam failure, and still remained at the time of sampling in August
218 2015³⁷.

219 Filtered V concentrations for most of the pore waters are positively correlated with filtered
220 concentrations of Fe, Al, Cr, Ni and Si, and slightly positive but flatter correlations with filtered Ca
221 concentrations (Figure 4). By contrast, filtered concentrations of inflow waters are poorly correlated
222 with Fe, Al and Ni, but show good correlations with Si, Ca and Cr, together with some of the pore
223 water samples.

224 The PHREEQC modeling suggested that no minerals with V as a major component were
225 oversaturated in any of the Hazeltine Creek waters (Supplementary Table S1). Calcite, diasporite and
226 gibbsite were predicted to be slightly oversaturated in many of the samples (Supplementary Table
227 S1). Pentavalent V was predicted to form 100% of all of the aqueous V species in all but one (HC9)

228 of the stream waters. By contrast, the inflow and pore waters are modeled to contain varying amounts
229 of V(III) and V(V) (Supplementary Table S2. V(III) is modelled to dominate in some of the inflow
230 waters and in the pore waters at 20 cm depth, and V(V) is predicted to dominate in the majority of
231 the inflow waters and in the pore waters at 0 and 10 m depth (Supplementary Table S2). The
232 modelling suggests that HVO_4^{2-} was the dominant species (50-86%) in all but one (HC9) of the stream
233 waters, with lesser amounts of H_2VO_4^- (14-50%; (Supplementary Table S3). The inflow and pore
234 waters have relatively low calculated proportions of HVO_4^{2-} (inflow 23-63%, pore 21-46%) and
235 relatively high proportions of H_2VO_4^- (inflow 37-77%, pore 54-77% Supplementary Table S3). The
236 highest V concentrations recorded in this study occur in inflow and pore waters with $\text{pH} < 8.1$ -8.3,
237 which is the equilibrium point between the weak acid and conjugate base (pK_a) ($\text{pH} 8.1$ to 8.3)
238 between HVO_4^{2-} and H_2VO_4^- at 25°C ^{9,46}.

239 We did not measure DOC concentrations and thus were not able to develop a V-organic
240 complexation model. However, we acknowledge that V is known to bind with DOC in the form of
241 humic acids and EDTA in aquatic environments^{47,48,49} and therefore, that DOC may have played a
242 role in V cycling in the Hazeltine Creek catchment.

243 **Solid-phase V geochemistry and mineralogy.** Concentrations of V in the study samples
244 from 51 to 231 mg/kg (Supplementary Table S4), which are mostly within the range for Mount Polley
245 tailings collected in 2014²⁶. The V concentrations are lower than concentrations reported for some
246 mine wastes (e.g. 860-963 mg/kg for red mud from the 2010 Ajka, Hungary, alumina processing
247 repository failure⁴⁴), but are within the same range as others (e.g., 135 mg/kg V for abandoned Au
248 mine tailings, Nova Scotia, Canada⁵⁰; 40.7 mg/kg V for polysulfide tailings, Boliden, Sweden⁵¹). The
249 spilled tailings (samples POL-5- to 7, POL-9; Supplementary Table S5) are dominated by orthoclase
250 and albite (both 32-41 area %), with lesser amounts of hornblende/augite (3.9-5.1 area %), epidote
251 (3.5-4.9 area %), muscovite (3.2-3.8 area %), plagioclase (1.6-2.5 area %), quartz (1.3-2.4 area %)
252 and chlorite (1.3-1.5 area %), similar to proportions found by Kennedy et al.⁵². Magnetite abundance
253 is ascribed to Fe oxides in the automated mineralogy analysis, forming 1.2-3.1 area % of the total

mineralogy, while titanite forms 0.5-1.7 area %. A Cu-bearing Fe oxide phase containing >0.1 wt. % Cu was added to the automated mineralogy library³⁴, and this phase forms 0.5-2.3 area % of the tailings. The remaining samples (POL-12 to -14; Supplementary Table S5) contain higher proportions of quartz (20-50 area %), suggesting dilution by catchment soils.

Magnetite and titanite in the Mount Polley tailings both contain V (Figure 5), but no other tailings minerals were found to contain V at the detection limit of the microprobe (0.001 wt. %). Average V concentrations for 11 magnetite grains are 0.28 wt. % (range 0.16-0.37 wt. %), and for 14 titanite grains are 0.25 wt. % (0.14-0.35 wt. %). The latter are within the same order of magnitude to those determined by Celis⁵³ for 57 titanite grains from the Mount Polley deposit (mean 0.15 wt. % V, range 0.06-0.29 wt. % V). The magnetite also contain trace amounts of Si (mean 0.045 wt. %), and magnetite and titanite contain trace concentrations of Al (0.045 wt. % and 0.037 wt. %, respectively), Cr (0.042 wt. % and 0.001 wt. %, respectively) and Mn (0.13 wt. % and 0.042 wt. %, respectively). Vanadium concentrations in the Fe oxyhydroxide collected from a seep draining a re-profiled stream bank are low, at or below the limit of detection of the microprobe (≤ 0.001 wt. % V; 10 grains).

Vanadium XANES Analysis. Charaund et al.⁴³ proposed an elegant system for interpreting V K-edge XANES spectra based on the detail observation of pre-edge peak intensity and energy position. In this system, data are described in terms of variation in both co-ordination symmetry and valance state. Data are provided from multiple V(V) standards as V K-edge XANES is sensitive to changes in both valance and the mode of structural incorporation (e.g. V(V) on FeOOH is tetrahedral and V(V) in V_2O_5 is square pyramidal⁵⁴⁻⁵⁶). The multiple V(V) standards are therefore desirable in order to investigate the mode of V occurrence in samples. When the Mount Polly magnetite and titanite data are plotted in this scheme the sample data plots between the octahedral V^{3+} and V^{4+} standards. The magnetite samples appear to contain primarily V^{3+} , suggesting incorporation of V^{3+} via substitution for octahedral Fe^{3+} within the structure. This is consistent with other studies on magnetite⁵⁷⁻⁵⁹, although Balan et al.⁵⁸ also found minor (<10 %) V(IV) occupying octahedral sites. The Mount Polley titanite V plots between octahedrally co-ordinated V^{3+} and V^{4+}

(Figure 6), suggesting that it most likely substituting for octahedrally co-ordinated Fe^{3+} , Al^{3+} or Ti^{4+} in the mineral structure. Celis⁵³ found that Mount Polley titanite contained almost equal concentrations of Al and Fe, substantiating the possibility of V^{3+} substitution for Fe^{3+} and Al^{3+} . Pan and Fleet⁶⁰ also reported that octahedrally co-ordinated V^{3+} and V^{4+} had similar radii to octahedrally co-ordinated Al^{3+} (0.64, 0.58, 0.535 Å, respectively⁶¹) and could therefore substitute for the latter within the vanadian titanite of the Hemlo gold deposit.

The V-bearing iron oxyhydroxide sample plots between V^{4+} (O_h) and the V^{5+} absorbed to FeOOH standards. It is possible that V in these samples is present as a mixture between the primary V^{4+} and V^{5+} in absorption complexes on hydrous iron oxyhydroxides. However, adsorbed V^{4+} does not persist in oxygenated environments as it is readily oxidized to V^{5+} ⁶², and most of the scientific literature reports the strong affinity of Fe oxyhydroxides such as goethite and ferrihydrite to V^{5+} ^{54,64,65}. Kaur et al.⁶⁵ attempted to make samples of V(III)-containing goethite, but found that some oxidation occurred, and that V(III), V(IV) and V(V) were also present. The resultant XANES spectra are intermediate between V(III) and V(V), similar to our spectra (Figure 6). Kaur et al.⁶⁵ also provided data that suggested that oxidized V was not readily incorporated in the goethite, and therefore are likely present as adsorbed V(V) that was more easily removed by protons than more reduced forms.

Vanadium Cycling in Hazeltine Creek Following the Mount Polley Tailings Dam Failure and Remediation. V(III)-bearing magnetite and V(III) and/or V(IV)-bearing titanite (Figure 5, 6) were deposited within remobilized tailings and together with a large number of uprooted trees in the Hazeltine Creek catchment following the 2014 Mount Polley dam failure. It is also possible that lesser amounts of these minerals occurred within Hazeltine Creek channel and floodplain sediments and soils prior to the failure, given the relatively high V concentrations of some background soils²⁶. A year after the tailings dam failure high filtered concentrations of V in pore waters occurring at 20 cm and especially 10 cm depth in Hazeltine Creek, coincide with peak concentrations in Al, As, Ca, Cu, Fe, K, Mg, Mn, Ni, Zn and Si, and declines in ORP and pH (Figure 3). It is possible that these high

306 concentrations reflect those in initial tailings dam pore waters transported with the spilled tailings,
307 but this is unlikely for the following reasons. First, most of the tailings and interstitial water went into
308 Quesnel Lake rather than Hazeltine Creek²⁵, second, we sampled in a very disturbed mixed river
309 sediment rather than undisturbed layers of tailings and third, we sampled a year after the spill and the
310 nature of the channel (high gradient, gravelly substrate) encouraged flushing by hyporheic exchange.
311 Therefore, we propose that the high filtered V concentrations at 10 and 20 cm depth arose from
312 dissolution of V-bearing phases containing these elements just below the water-sediment interface⁶⁶.
313 Positive trends between concentrations of V and those of Al, Fe, Cr, Mn and Si (Figure 4) suggest
314 that one of the phases undergoing such dissolution could be the Mount Polley magnetite which
315 incorporates these elements. The dissolution of vanadium titano-magnetite with similar
316 concentrations of V (0.28 wt. %) has been demonstrated experimentally by Hu et al.¹⁰, who showed
317 that V is released from magnetite between pH 5.9 and 8.8 under dissolved O₂ ranging from 5% to
318 80%. Other possibilities for phases undergoing dissolution to produce these positive trends could be
319 V-bearing clay minerals, Al(OH)₃ or Fe-Al-Mn-Si oxyhydroxides whose V concentrations were
320 below detection limits of our microprobe analysis and which were small enough to pass through the
321 0.45 µm filter.

322 Vanadium concentrations in inflow waters are mostly lower than those in pore waters, and
323 those up to 50 µg/L correlate well with Ca, Si, Fe and Al, while those up to 25 µg/L correlate with
324 Cr and Mn (Figure 4). The released Ca and Si can be attributed to the weathering of epidote or feldspar
325 which occur in the tailings, and that of Ca, Si, Fe and Al, to the weathering of hornblende
326 (Supplementary Table S5), but none of these minerals were found to contain V. Ca and Si are two of
327 the major components of titanite, and Mount Polley titanites contain trace amounts of V, Fe, Al, Cr
328 and Mn. It is proposed that titanite weathering in the tailings piles from which the inflows emanate is
329 responsible for these trends and modest enrichments in V. Although they did not analyze for V, Tilley
330 and Eggleton⁶⁷ have shown that titanite can weather, likely under supergene conditions, to beidellite
331 and anatase at neutral pH, resulting in loss of all of the Ca but retention of Ti. The reason for the

different V-trends shown by the inflows and pore waters (Figure 4) is unknown but may be related to different proportions of these minerals in the spilled tailings.

Positive saturation indices for ferrihydrite and goethite (Supplementary Table S1), the presence of Fe oxyhydroxides forming along the inflow waters and the sampled V-bearing Fe oxyhydroxide (POL-13, Supplementary Table S5, Supplementary Figure S3; Figure 5) show that some of the mobilized V is taken up by secondary Fe precipitates. Iron oxyhydroxides were observed in 2015 at the sediment-water interface in Hazeltine Creek, especially in the riparian area downstream of the second gorge where the gradient shallowed and the valley widened (near HC-9; Figure 1). These, and the declines in Fe concentrations in the Hazeltine Creek stream waters at 0 cm in the depth profiles collected (Figure 3) suggests that the high Fe pore waters at 10 cm depth were attenuated either by diffusion of aqueous V and Fe, and/or by precipitation of Fe oxyhydroxides at this interface. The V in these Fe phases is most likely to be V(V), given the dominances of this species in the stream waters, in most of the inflow waters and in the pore waters at 0 and 10 cm depth in the PHREEQC (Supplementary Table S2), and in the XANES modeling (Figure 6). The fact that filtered V concentrations for samples with pH values between 7.5 and 8.3 are higher than those with pH values greater than 8.3 (Supplementary Figure S1) is consistent with experimental studies. Dzombak and Morel⁶⁸ and Naeem et al.⁸ demonstrated that V sorption to Fe oxides and hydroxides was highest between pH c. 3 and 3.5 and then decreased as pH increased from 4 to 11.6. Naeem et al.⁸ attributed this decrease to competition between OH⁻ and aqueous V anions for Fe oxide/hydroxide surface binding sites. Similarly, positive saturation indices for the Al oxyhydroxide diaspore and Al hydroxide gibbsite, and positive trends between total Al, Si and V concentrations (Supplementary Figure S2), also suggest that the formation of secondary phases such as (Al-Si-bearing) Fe oxyhydroxides, Al oxyhydroxides and hydroxides or clay minerals (see above) may attenuate aqueous V concentrations that show a decline downstream in Hazeltine Creek (Figure 2).

The association of V with Fe oxyhydroxides has been observed for streams throughout Sweden affected by natural and anthropogenic inputs of V⁶⁹, with other studies showing that

358 considerable transport occurs in the colloidal phase⁷⁰. Concentrations of total V in Hazeltine Creek
359 are higher than those of filtered V (Figure 2), and apart from three inflow water samples, total Fe, Al
360 and Si concentrations correlate well with total V concentrations (Supplementary Figure S2),
361 suggesting that fine particulate transport of V is significant in the catchment.

362 The significance of the Mount Polley tailings spill on water quality and V transport are
363 illustrated in Figure S4 where V flux (kg yr^{-1}) and yield ($\text{kg km}^{-2} \text{yr}^{-1}$) are compared to unaffected
364 regional watersheds in British Columbia and other mining-affected watercourses around the world.
365 Transport of V in the stream is elevated compared to nearby regional streams, even when the flux
366 data are weighted by watershed area. In addition, under high flow conditions, V yield (measured at
367 HC-9 in 2016) was comparable to (low flow) yield values recorded in Torna Creek, Hungary,
368 following the 2010 Ajka bauxite residue tailings spill⁷¹. The V transport data reported here show a
369 larger departure from background concentrations and fluxes than those reported for Cu at Mount
370 Polley³⁷. Particulate transport of V appeared to be more dominant under high flow than low flow,
371 suggesting physical mobilization of residual tailings could be an important transport mechanism for
372 V during spring freshets and summer rainfall-runoff events. However, the bulk of the tailings
373 remaining after our sampling in 2015 and 2016 were removed from the Hazeltine Creek watershed
374 and returned to the tailings storage facility (L. Anglin, pers. comm., 2018), suggesting that the effects
375 of such physical mobilization could be minimal in the future.

376 The weathering of mine tailings derived from dam failures such as Mount Polley can play a
377 major role in V cycling in surficial environments. We have presented evidence that deposition of V-
378 bearing tailings can lead to enhanced pore and inflow water V concentrations, especially when
379 deposited or stored in environments where dissolution of primary (e.g. V-bearing magnetite and
380 titanite) and secondary (V-bearing Fe and Al oxyhydroxides or clay) minerals also leads to greater V
381 mobilization. However, these enhanced V concentrations can be naturally attenuated, and their
382 potential ecotoxicity reduced, by formation of secondary colloidal Fe oxyhydroxides that reduce
383 aqueous V to near background levels.

384

385 **Supporting Information**

386 Detailed water sampling and XANES methods and mineral results, pore water geochemical data,
387 PHREEQC modelling results and plots, automated mineralogy data and V flux and yield plot. This
388 material is available free of charge via the Internet at <http://pubs.acs.org>.

389

390 **AUTHOR INFORMATION**391 **Corresponding Author**

392 E-mail: k.hudson-edwards@exeter.ac.uk; phone: +44 1326 259 489.

393

394 **Notes**

395 The authors declare no competing financial interests.

396

397 **ACKNOWLEDGEMENTS**

398 We thank Lyn Anglin, Colleen Hughes, Art Frye and Shauna Litke of Mount Polley Mining
399 Corporation for providing site information and data, and for field support and access. We extend
400 our special thanks to Lyn Anglin for reviewing an early version of the manuscript. We also
401 acknowledge Phil Riby, Andy Beard, Agatha Dobosz and Patrizia Onnis for technical support. We
402 thank Diamond Light Source for access to beamline I18 (proposal SP15046), and Konstantin
403 Ignatyev (Station Scientist Diamond Light Source Ltd.) for support that contributed to the results
404 presented here. We are also grateful to the three anonymous reviewers and Associate Editor Daniel
405 Giammar whose comments significantly improved the manuscript. This research was funded by the
406 UK Natural Environment Research Council (grant NE/M017486/1).

407

408 **REFERENCES**

- 409 (1) Kabata-Pendias, A. Trace Elements in Soils and Plants, 4th ed. CRC Press, Boca Raton, FL,
410 2011.
- 411 (2) Imtiaz, M.; Rizwan, M. S.; Xiong, S.; Li, H.; Ashraf, M.; Shahzad, S. M.; Shahzad, M.; Rizwan,
412 M.; Tu, S. Vanadium, recent advancements and research prospects: a review. *Environ. Int.* **2015**
413 *80*, 79-88.
- 414 (3) Goldwasser, I.; Gefel, D.; Gershonov, E.; Fredkin, M.; Schechter, Y. Insulin-like effects of
415 vanadium: basic and clinical implications. *J. Inorg. Biochem.* **2000** *80*, 21-25.
- 416 (4) McCrindle, C. M. E.; Mokantla, E.; N. Duncan, N. Peracute vanadium toxicity in cattlegrazing
417 near a vanadium mine. *J. Environ. Monit.* **2001** *3*, 580-582.
- 418 (5) Yang, J.; Teng, Y.; Wu, J.; Chen, H.; Wang, G.; Song, L.; Yue, W.; Zuo, R.; Zhai, Y. Current
419 status and associated human health risk of vanadium in soil in China. *Chemosphere* **2017** *171*,
420 635-643.
- 421 (6) Evangelou, A. M. Vanadium in cancer treatment. *Crit. Rev. Oncol.* **2002** *42*, 249-265.
- 422 (7) Leonard, A.; Gerber, G. Mutagenicity, carcinogenicity, and teratogenicity of vanadium, Adv.
423 *Environ. Sci. Technol.* **1998** *31*, 143-149.
- 424 (8) Naeem, A.; Westerhoff, P.; Mustafa, S. Vanadium removal by metal (hydr)oxide adsorbents.
425 *Water Res.* **2007** *41*(7), 1596-1602.
- 426 (9) Huang, J. -H.; Huang, F.; Evans, L.; Glasauer, S. Vanadium: Global (bio)geochemistry. *Chem.*
427 *Geol.* **2015** *417*, 8-89.
- 428 (10) Hu, X.; Yuyan, Y.; Peng, X. Release kinetics of vanadium from vanadium titano-magnetite:
429 The effects of pH, dissolved oxygen, temperature and foreign ions. *J. Environ. Sci.* **2018** *64*, 28-
430 305.
- 431 (11) Environment and Climate Change Canada. Canadian Environmental Protection Act, 1999.
432 Federal Environmental Quality Guidelines. Vanadium, 2016. Available on [http://www.ec.gc.ca/ese-](http://www.ec.gc.ca/ese-ees/default.asp?lang=En&n=48D3A655-1)
433 [ees/default.asp?lang=En&n=48D3A655-1](http://www.ec.gc.ca/ese-ees/default.asp?lang=En&n=48D3A655-1), accessed 11/1/2019.

- 434 (12) Schiffer, S.; Liber, K. Estimation of vanadium water quality benchmarks for the protection of
435 aquatic life with relevance to the Athabasca Oil Sands region using species sensitivity distributions.
436 *Environ. Toxicol. Chem.* **2017** *36*, 3034-3044.
- 437 (13) Agency for Toxic Substances and Disease Registry (ATSDR). Toxicological profile for
438 vanadium. U.S. Department of Health and Human Services, Public Health Service. Available on
439 <https://www.atsdr.cdc.gov/toxprofiles/tp58.pdf>, 2012, accessed 2 July 2018.
- 440 (14) Jensen-Fontaine, M.; Norwood, W. P.; Brown, M.; Dixon, D. G.; Le, X. C. Uptake and
441 speciation of vanadium in the benthic invertebrate *Hyalella Azteca*. *Environ. Sci. Technol.* **2014**
442 *48*, 731-738.
- 443 (15) Mišík, M.; Burke, I. T.; Reismüller, M.; Pichler, C.; Rainer, B.; Mišíková, K.; Mayes, W. M.;
444 Snasmueller, S. Red mud a byproduct of aluminum production contains soluble vanadium that
445 causes genotoxic and cytotoxic effects in higher plants. *Sci. Total Environ.* **2014** *493*, 883-890.
- 446 (16) Nriagu, J.; Pirrone, N. Emission of vanadium into the atmosphere, In Nriagu, J. (Ed.)
447 *Vanadium in the Environment, Part I: Chemistry and Biochemistry*; Wiley, New York, pp. 25-
448 36, 1988.
- 449 (17) Shotyk, W.; Belland, R.; Duke, J.; Kempter, H.; Krachler, M.; Noernberg, T.; Pelletier, R.;
450 Vile, M. A.; Wieder, K.; Zacccone, C.; Zhang, S., Sphagnum mosses from 21 ombrotrophic bogs
451 in the Athabasca bituminous sands region show no significant atmospheric contamination of
452 "heavy metals". *Environ. Sci. Technol.* **2014** *48*, 12603-12611.
- 453 (18) Yang, J.; Tang, Y.; Yang, K.; Rouff, A. A.; Elzinga, E. J.; Huang, J. H. Leaching
454 characteristics of vanadium in mine tailings and soils near a vanadium titanomagnetite mining
455 site. *J. Hazard. Mat.* **2014** *264*, 498-504.
- 456 (19) Cao, X.; Diao, M.; Zhang, B.; Liu, H.; Wang, S.; Yang, M. Spatial distribution of vanadium
457 and microbial community responses in surface soil of Panzhihua mining and smelting area,
458 China. *Chemosphere* **2017** *183*, 9-17.

- 459 (20) Watt, J. A. J.; Burke, I. T.; Edwards, R. A.; Malcom, H. M.; Mayes, W. M.; Olszewska, J. P.;
460 Pan, G.; Graham, M. C.; Heal, K. V.; Rose, N. L.; Turner, S. D.; Spears, B. M. Vanadium: A re-
461 emerging environmental hazard. *Environ. Sci. Technol.* **2018** *52*, 11973-11974.
- 462 (21) Burke, I. T.; Peacock, C. L.; Lockwood, D. I.; Stewart, R. J. G.; Mortimer, M. B.; Ward, P.;
463 enforth, K.; Bruiz, W. M. Behavior of aluminum, arsenic, and vanadium during the
464 neutralization of red mud leachate by HCl, gypsum, or seawater. *Environ. Sci. Technol.* **2013** *47*,
465 6527-6535.
- 466 (19) Kossoff, D.; Dubbin, W. E.; Alfredsson, M.; Edwards, S. J.; Macklin, M. G.; Hudson-Edwards,
467 K. A. Mine tailings dams: Characteristics, failure, environmental impacts, and remediation. *Appl.*
468 *Geochem.* **2014** *51*, 229-245.
- 469 (23) WISE World Information Service on Energy Uranium Project, 2018, Chronology of Major
470 Tailings Dam Failures <http://www.wise-uranium.org/mdaf.html> (accessed 3 July 2018).
- 471 (24) Petticrew, E. L.; Albers, S. J.; Baldwin, S. A.; Carmack, E. C.; Dery, S. J.; Gantner, N.;
472 Graves, K. E.; Laval, B.; Morrison, J.; Owens, P. N.; Selbie, D. T.; Vagle, S. The impact of a
473 catastrophic mine tailings impoundment spill into one of North America's largest fjord lakes:
474 Quesnel Lake, British Columbia, Canada. *Geophys. Res. Lett.* **2015** *42*, 3347-3355.
- 475 (25) L. Nikl, B. Wernick, J. Van Geest, C. Hughes, K. McMahan, L. Anglin, L., Mount Polley Mine
476 embankment breach: Overview of aquatic impacts and rehabilitation. Proceedings Tailings and
477 Mine Waste 2016, Keystone, Colorado, 2-5 October 2016, pp. 845-856.
- 478 (26) SNC-Lavalin Inc Mount Polley Mining Corporation post-event environmental impact
479 assessment report, Appendix A: Hydrotechnical and geomorphological assessment, 621717;
480 2015.
- 481 (27) Independent Expert Engineering Investigation and Review Panel, Report on Mount Polley
482 Tailings Storage Facility Breach, 2015.

- 483 (28) MPMC, Mount Polley Mining Corporation post-event environmental impact assessment report
484 - Key findings report. Report No. Available at [https://www.imperialmetals.com/assets/docs/mt-](https://www.imperialmetals.com/assets/docs/mt-polley/2015-06-18-MPMC-KFR.pdf)
485 [polley/2015-06-18-MPMC-KFR.pdf](https://www.imperialmetals.com/assets/docs/mt-polley/2015-06-18-MPMC-KFR.pdf), 2015.
- 486 (29) Golder Associates Ltd Mount Polley Mining Corporation post-event environmental impact
487 assessment report, Appendix F: Mount Polley Tailings Dam Failure - Surface Water Quality
488 Impact Assessment, 1411734-036-R-Rev0-10000, 2015, pp. 1653-1984.
- 489 (30) Hudson-Edwards, K. A.; Macklin, M. G.; Jamieson, H. E.; Brewer, P. A.; Coulthard, T. J.;
490 Howard, A. J.; Turner, J. N. The impact of tailings dam spills and clean-up on sediment and
491 water quality in river systems: The Ríos Agrio-Guadiamar, Aznalcóllar, Spain. *Appl. Geochem.*
492 **2003** *18*, 221-239.
- 493 (31) Bird, G.; Brewer, P. A.; Macklin, M. G.; Balteanu, D.; Serban, M.; Driga, B.; Zaharia, S. River
494 system recovery following the Novat-Rosu tailings dam failure, Maramures County, Romania,
495 *Appl. Geochem.* **2008** *23*, 3498-3518.
- 496 (32) Golder Associates Inc, Mount Polley rehabilitation and remediation strategy – Detailed site
497 investigation Mount Polley tailings dam failure Mount Polley, BC. (Report No. 1411734-114-R-
498 Rev0-11000), 2016.
- 499 (33) Golder Associates Ltd Mount Polley Mining Corporation post-event environmental impact
500 assessment report, Appendix I: Mount Polley Tailings Dam Failure - Post-event Water Quality
501 August 2014 through April 2015, 25 p.; 2015.
- 502 (34) Minnow Environmental Inc, Mount Polley Mining Corporation Post-even Environmental
503 Impact Assessment Report (Appendix E: Mount Polley mine tailings dam failure: Sediment
504 quality impact characterization), 2015.
- 505 (35) SRK Consulting (Canada) Inc, Mount Polley Mine Tailings Dam Failure: Update on
506 Geochemical Characterization of Spilled Tailings (Vancouver, Canada), 2015.

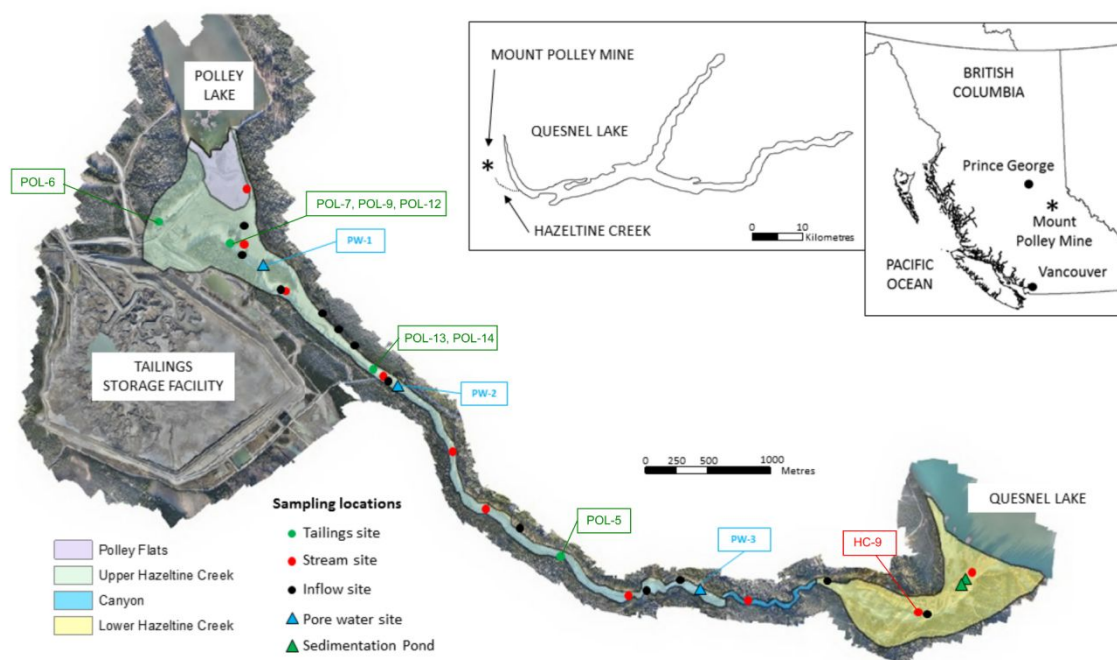
- 507 (36) SRK Consulting (Canada) Inc Mount Polley Mining Corporation post-event environmental
508 impact assessment report. Appendix C: Mount Polley Tailings Dam Failure - Geochemical
509 characterisation of spilled tailings, 1CI008.003, 2015.
- 510 (37) Byrne, P.; Hudson-Edwards, K. A.; Bird, G.; Macklin, M. G.; Brewer, P. A.; Williams, R D.;
511 Jamieson, H. E. Water quality impacts and river system recovery following the 2014 Mount
512 Polley mine tailings dam spill, British Columbia, Canada. *Appl. Geochem.* **2018** *91*, 64-74.
- 513 (38) McMillan, W. J. Porphyry deposits of the Canadian cordillera. *Geosci. Can.* **1996** *23*, 125-134.
- 514 (39) Minnow Environmental Inc., Mount Polley Mine Aquatic Environmental Characterization -
515 2007, 2009.
- 516 (40) Ball, J. W.; Nordstrom, D. K. User's manual for WATEQ4F, with revised thermodynamic
517 database and test cases for calculating speciation of major, trace, and redox elements in natural
518 waters. U.S. Geol. Surv. Open-File Rep. 1991, 91-183, 189.
- 519 (41) Parkhurst, D. L.; Appelo, C. A. J. Description of input and examples for PHREEQC version 3:
520 a computer program for speciation, batch-reaction, one-dimensional transport, and inverse
521 geochemical calculations. US Geological Survey Techniques and Methods, book 6, chap. A43,
522 497 p.; 2013.
- 523 (42) Ravel, B. Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray
524 absorption spectroscopy using IFEFFIT. *J. Synchrotron Radiat.* **2005** *12*, 537-541.
- 525 (43) Chaurand, P.; Rose, J.; Brion, V.; Salome, M.; Proux, O.; Nassif, V.; Olivi, L.; Susini, J.;
526 Hazemann, J. -L.; Bottero, J. -Y. New methodological approach for the vanadium K-edge X-ray
527 absorption near-edge structure interpretation: Application to the speciation of vanadium in oxide
528 phases from steel slag. *J. Phys. Chem. B* **2007** *111*, 5101-5110.
- 529 (44) Burke, I. T.; Mayes, W. M.; Peacock, C. L.; Brown, A. P.; Jarvis, A. P.; Bruiz, K. Speciation
530 of arsenic, chromium, and vanadium in red mud samples from the Ajka spill site, Hungary, *Environ.*
531 *Sci. Technol.* **2012** *46*, 3085-3092.

- (45) Shiller, A. M.; Boyle, E. A. Dissolved vanadium in rivers and estuaries. *Earth Planet. Sci. Lett.* **1987** *86*, 214-224.
- (46) Wright, M. T.; Stollenwerk, K. G.; Belitz, K. Assessing the solubility controls on vanadium in groundwater, northeastern San Joaquin Valley, CA. *Appl. Geochem.* **2014** *48*, 41-52.
- (47) Wehrli, B.; Stumm, W. Vanadyl in natural waters: Adsorption and hydrolysis promote oxygenation. *Geochim. Cosmochim. Acta* **1989** *53*, 69-77.
- (49) Lu, X.Q.; Johnson, W.D.; Hook, J. Reaction of vanadate with aquatic humic substances: an ESR and V-51 NMR study. *Environ. Sci. Technol.* *32*, 2257-22263.
- (50) Levshina, S. An assessment of metal-humus complexes in river waters of the Upper Amur basin, Russia. *Environ. Monit. Assess.* **2018** *190*, 18.
- (50) Wong, H. K. T., Gauthier, A.; Nriagu, J. O. Dispersion and toxicity of metals from abandoned gold mine tailings at Goldenville, Nova Scotia, Canada. *Sci. Total Environ.* **1999** *228*, 35-47.
- (51) Gleisner, M.; Herbert, R. B. Sulfide mineral oxidation in freshly processed tailings: batch experiments. *J. Geochem. Explor.* **2002** *76*, 139-153.
- (52) Kennedy, C. B.; Day, S. J.; Anglin, C. D. Geochemistry of tailings from the Mount Polley Mine, British Columbia, Proceedings Tailings and Mine Waste 2016, Keystone, Colorado, USA, 2-5 October 2016, pp. 857-868.
- (53) Celis, A. Titanite as an indicator mineral for alkalic porphyry Cu-Au deposits in south-central British Columbia, UBC Library, doi 10.14288/1.0166663, 2015.
- (54) Peacock, C. L.; Sherman, D. M. Vanadium(V) adsorption onto goethite (α -FeOOH) at pH 1.5 to 12: a surface complexation model based on ab initio molecular geometries and EXAFS spectroscopy. *Geochim. Cosmochim. Acta* **2004** *68*, 1723-1733.
- (55) Chaurand, P.; Rose, J.; Briois, V.; Salome, M.; Proux, O.; Nassif, V.; Olivi, L.; Susini, J.; Hazemann, J. -L.; Bottero, J. -Y. New methodological approach for the vanadium K-edge X-ray absorption near-edge structure interpretation: Application to the speciation of vanadium in oxide phases from steel slag. *J. Phys. Chem. B* **2007** *111*, 5101 – 5110.

- (56) Hobson A. J.; Stewart D. I.; Bray A. W.; Mortimer R. J. G.; Mayes W. M.; Riley A. L.; Rogerson M.; Burke I. T. Behaviour and fate of vanadium during the aerobic neutralisation of hyperalkaline slag leachate. *Sci. Total Environ.* **2018** *643*, 1191-1199.
- (57) Toplis, M. J.; Corgne, A. An experimental study of element partitioning between magnetite, clinopyroxene and iron-bearing silicate liquids with particular emphasis on vanadium. *Contrib. Mineral. Petrol.* **2002** *144*, 22-37.
- (58) Balan, E.; de Villiers, J. P. R.; Eeckhout, S. G.; Glatzel, P.; Toplis, M. J.; Fritsch, E.; Allard, T.; Galois, L.; Calas, G. The oxidation state of vanadium in titanomagnetite from layered basic intrusions. *Am. Mineral.* **2006** *91*, 953-956.
- (59) Canil, D.; Grondahl, C.; Lacourse, T.; Pisiak, L. K. Trace elements in magnetite from porphyry Cu-Mo-Au deposits in British Columbia, Canada. *Ore Geol. Rev.* **2016** *72*, 1116-1128.
- (60) Pan, Y.; Fleet, M. E. Vanadium-rich minerals of the pumpellyite group from the Hemlo gold deposit, Ontario. *Can. Mineral.* **1992** *30*, 153-162.
- (61) Shannon, R. D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.* **1976** *A32*, 751-767.
- (62) Wehrli, B.; Stumm, W. Vanadyl in natural waters - Adsorption and hydrolysis promote oxygenation. *Geochim. Cosmochim. Acta* **1989** *53*, 69-7.
- (63) U. Schwertmann, U.; Pfab, G. Structural vanadium in synthetic goethite. *Geochim. Cosmochim. Acta* **1994** *58*, 4349-4352.
- (64) Larsson, M. A.; Persson, I.; Sjöstedt, C.; Gustafsson, J. P. Vanadate complexation to ferrihydrite: X-ray absorption spectroscopy and CD-MUSIC modelling. *Environ. Chem.* **2016** *14*, 141-150.
- (65) Kaur, N.; Singh, B.; Kennedy, B. J.; Gräfe, M. The preparation and characterization of vanadium-substituted goethite: The importance of temperature. *Geochim. Cosmochim. Acta* **2009** *73*, 582-593.

- 583 (66) Surridge, B. W. J.; Heathwait, A. L.; Baird, A. J. The release of phosphorus to porewater and
584 surface water from river riparian sediments. *J. Environ. Qual.* **2007** *36*, 1534-1544.
- 585 (67) Tilley, D. B.; Eggleton, R. A. Titanite low-temperature alteration and Ti mobility. *Clays Clay*
586 *Miner.* **2005** *53*, 100-107.
- 587 (68) Dzombak, D. A.; Morel, F. M. M. Surface Complexation Modelling: Hydrous Ferric Oxide.
588 Wiley-Interscience, New York, 1990.
- 589 (69) Wällstedt, T.; Björkvald, L.; Gustafsson, J. P. Increasing concentrations of arsenic and
590 vanadium in (southern) Swedish streams. *Appl. Geochem.* **2010** *25*, 1162-1175.
- 591 (70) Dahlgqvist, R.; Andersson, K.; Ingri, J.; Larsson, T.; Stolpe, B.; Turner, D. Temporal variations
592 of colloidal carrier phases and associated trace elements in a boreal river. *Geochim. Cosmochim.*
593 *Acta* **2007** *71*, 5339-5354.
- 594 (71) Mayes, W. M.; Jarvis, A. P.; Burke, I. T.; Walton, M.; Feigl, V.; Klebercz, O.; Gruiz, K.
595 Dispersal and attenuation of trace contaminants downstream of the Ajka bauxite residue (red mud)
596 depository failure, Hungary. *Environ. Sci. Technol.* **2011** *45*, 5147-5155.
- 597 (72) Hobson, A. J. Stewart, D. I.; Bray, A. W.; Mortimer, R. J. G.; Mayes, W. M.; Rogerson, M.;
598 Burke, I. T. Mechanism of vanadium leaching during surface weathering of basic oxygen
599 furnace steel slag blocks: A microfocus X-ray absorption spectroscopy and electron microscopy
600 study. *Environ. Sci. Technol.* **2017** *51*, 7823-7830.
- 601 (73) Bronkema, J. L.; Bell, A. T. Mechanistic studies of methanol oxidation to formaldehyde on
602 isolated vanadate sites supported on MCM-48. *J. Phys. Chem. C* **2007** *111*, 420-430.
- 603 (74) Wong, J.; Lytle, F. W.; Messmer, R. P.; Maylotte, D. H. K-edge absorption-spectra of selected
604 vanadium compounds. *Phys. Rev. B* **1984** *30*, 5596-5610.
- 605

607 **Figure 1.** Location of study area showing Hazeltine Creek stream (HC-), inflow sample, pore water
608 (PW-) and tailings, sediment and Fe oxyhydroxide (POL-) sample sites for materials collected in
609 2014 and 2015. Labels shown are for those samples discussed in this manuscript; sample locations
610 for the remaining stream, inflow and pore water samples are shown in Byrne et al.³⁷.



615 **Figure 2.** Spatial profile of Hazeltine Creek stream and inflow filtered (V-F) and unfiltered (V-T) V
616 concentrations. Samples were collected in August 2015. Pre-tailings dam spill median V
617 concentration of 1 $\mu\text{g/L}^{29}$ is shown for reference.

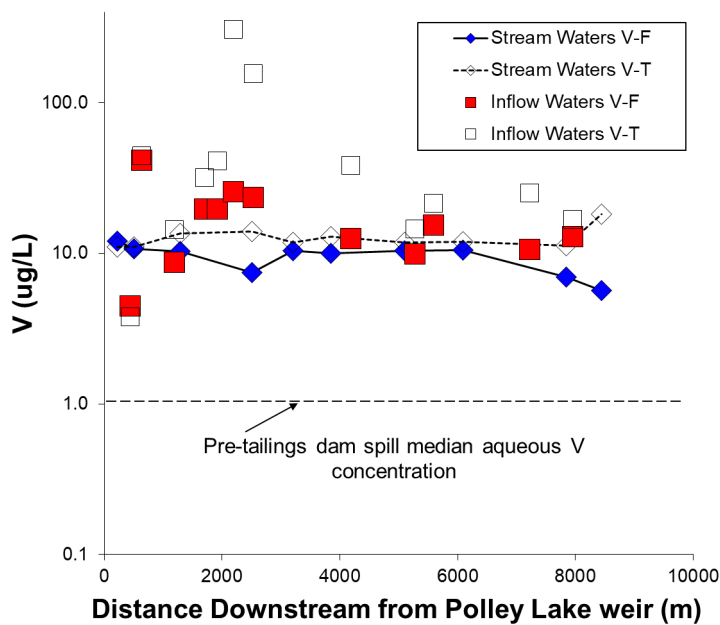
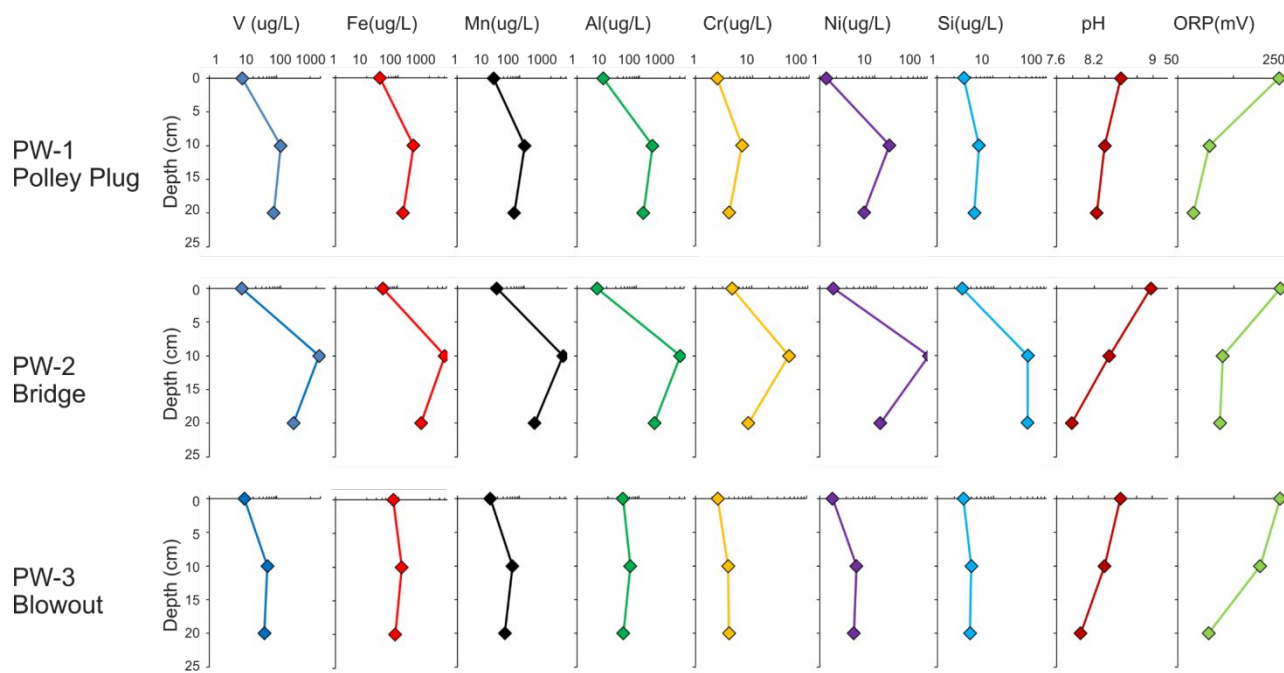
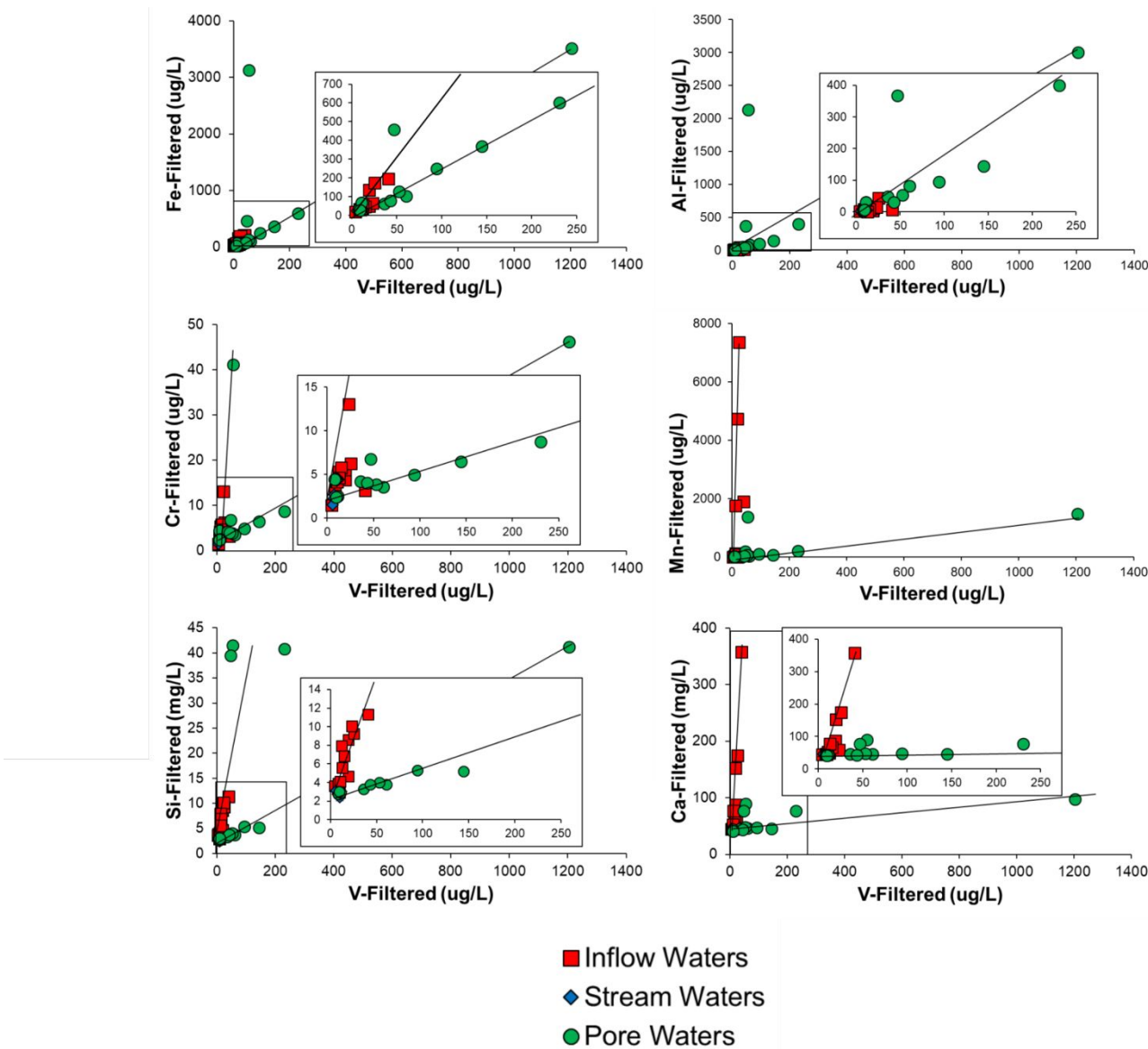


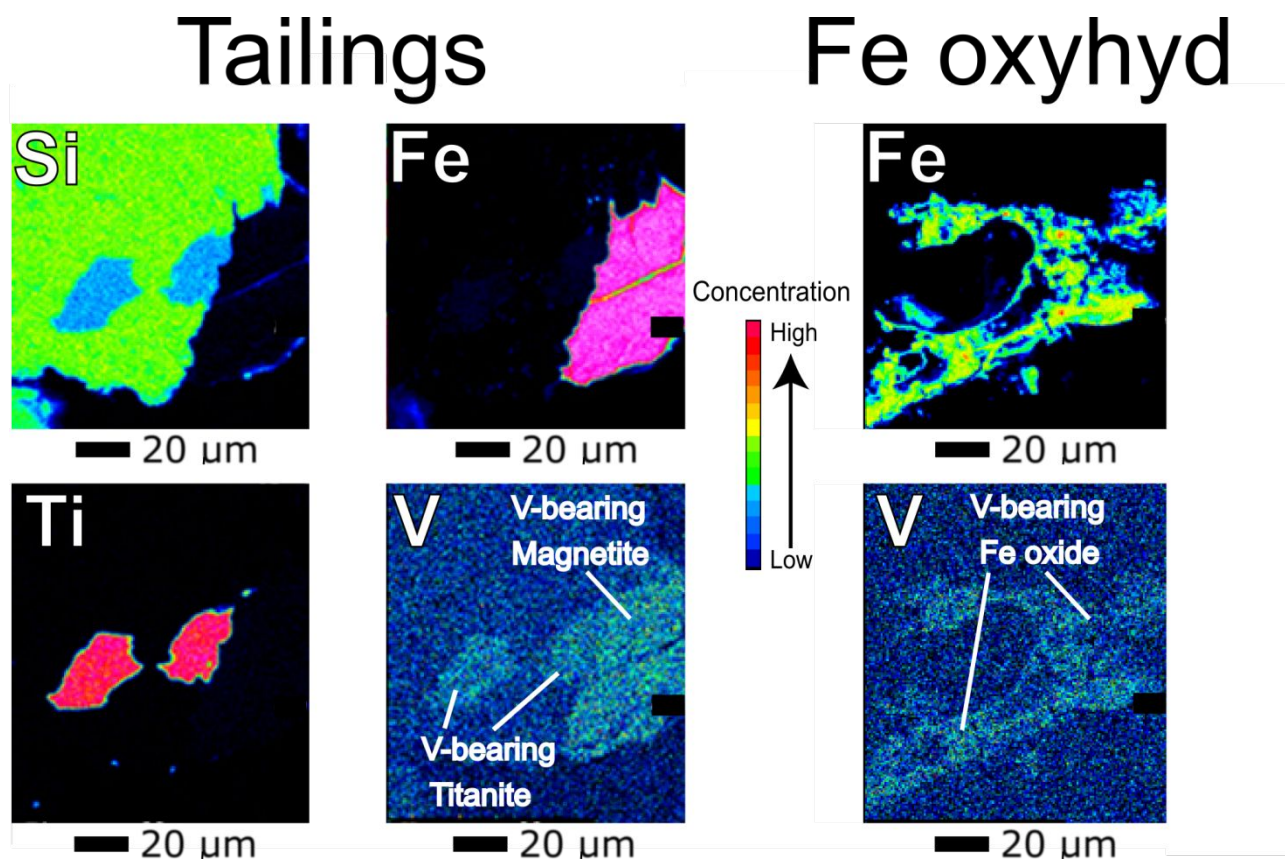
Figure 3. Geochemical profiles for pore water profiles PW-1, PW-2 and PW-3.

625 **Figure 4.** X-Y plots showing relationship between filtered V ($\mu\text{g L}^{-1}$) and other filtered element
626 concentrations in stream, inflow and pore waters. Stream water sample concentrations are mostly <
627 10 $\mu\text{g/L}$ so are masked by the inflow and pore waters. Trends shown for the inflow waters (red
628 squares) and for most of the pore water data (green circles).



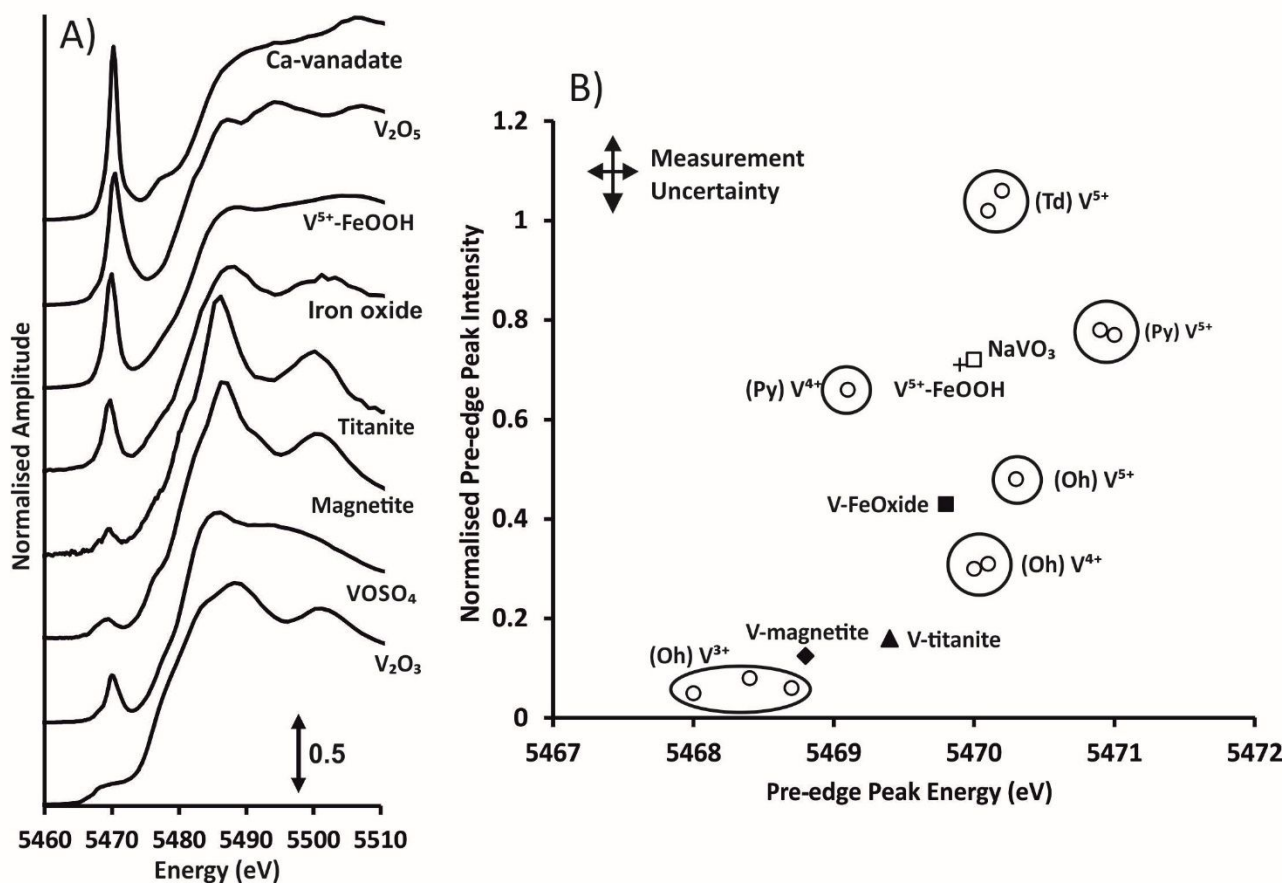
635 **Figure 5.** Electron microprobe X-ray maps showing V-bearing titanite and magnetite in Mount
636 Polley tailings (POL-5), and V-bearing Fe oxide in the Fe oxyhydroxide (Fe oxyhyd) (POL-13).

637



640 **Figure 6.** (a) K-edge XANES spectra collected from Mount Polly mineral samples and selected V-
641 containing standards. (b) Plot of pre-edge intensity vs. pre-edge peak energy derived from V K-edge
642 XANES spectra. V standard data from Hobson et al.⁷², Burke et al.^{21,44}, Charaund et al.⁴³, Bronkema
643 and Bell⁷³ and Wong et al.⁷⁴. (T_d), (P_y) and (O_h) refer to tetrahedral, square pyramidal and
644 octahedral co-ordination, respectively.

645



646
647